

**GEOCHEMICAL CORRELATION STUDY OF DEGRADED OILS AND
ROCKY BROOK SOURCE ROCKS, DEER LAKE BASIN**

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George S. Langdon and T. Abrajano, Jr.

**Centre for Earth Resources Research
Department of Earth Sciences
Memorial University of Newfoundland
St. John's, NF A1B 3X5**

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EXECUTIVE SUMMARY

A geochemical correlation study was undertaken to attempt to provide further information on the prospectivity of the Deer Lake Basin. Five samples were chosen for the geochemical analyses: of these, three samples were of dead oils (so called "bitumens") and two samples were from the Rocky Brook shales, which were considered source rock.

The study confirms that oil has been generated in the vicinity of the basin and has undergone migration into potential reservoir rocks. The highly degraded oil (bitumen) samples from the Goose Arm road do not yield enough information to allow correlation with source rocks, but the bitumen sample from drillcore in the Howley Formation is less degraded, and is tentatively correlated with the Rocky Brook shale samples, based on isotopic and gas chromatographic results. In general, the terrestrial geochemical character of the Howley bitumen points to its origin from lacustrine algae, given the lack of any landplant-dominated source rocks in the basin.

The two Rocky Brook samples are different from each other both in bulk and in isotopic composition, but both are lacustrine in origin.

INTRODUCTION

This study was completed for Vinland Petroleum Inc. as a contribution to its exploration program in the Deer Lake Basin of western Newfoundland. The purpose of this work was, firstly, to assess the significance of the numerous bitumen shows in and around the margins of the Deer Lake Basin (do these represent oil?), and, secondly, to compare and attempt to correlate between bitumens from outcrop and core (representing degraded oil) and the Rocky Brook shales (representing the source rock). As stated in the recommendations of the Langdon (1993) report on the petroleum potential of the basin, the main concern was whether or not the degraded bitumen could be typed and correlated, given its long exposure to oxidation and biodegradation.

The geochemical correlation study was undertaken, then, to attempt to confirm some of the predictions made in the Langdon report about the prospectivity of the basin. If a Carboniferous, *in situ* oil source rock could be established and correlated with known oil shows, the potential of the basin for oil accumulation would be quite high, given the recent increase in understanding of Carboniferous basins as self-contained, prolific oil-producers (e.g., Katz, 1990; other papers in this volume).

Five samples were chosen for the geochemical analysis: of these three samples were of dead oils (so called "bitumens") and two samples were from the Rocky Brook shales, which were considered source rock. Of the bitumen samples, Sample Bit-1 was taken from a large pure clump of dead oil taken from the test pit north of the Goose Arm Road, and Sample Bit-2 was taken from the centre of Goose Arm road. Sample D3-2 came from a depth of 42.5m in the D3 borehole, which lies just to the east of the Hampden fault in the northeastern sector of the basin. The two source rock samples, RB-8 and RB-25, came from depths of 76.5m in borehole A-3 and 117m in borehole A-5, respectively. These localities are described in the report of Langdon (November 8, 1993).

SAMPLE PREPARATION AND ANALYSIS

Crushing

All samples were collected from outcrop and core in western Newfoundland and prepared by the first author at the Centre for Earth Resources Research. The samples were crushed to a fine powder, packaged and submitted for analysis. Linda Winsor provided valuable advice to the first author and carried out the analyses under the direction of the second author.

Analytical Procedure

The extraction and purification procedure used in the processing of the samples is summarized graphically in Figure 1. Gas chromatographic analysis was carried out for the saturated and aromatic hydrocarbon fractions, and two sets of gas chromatograms were produced. For the saturate and aromatic fraction, compounds were identified from comparison of retention times of authentic standards. The resulting chromatograms show retention time on the horizontal axis plotted against intensity on the vertical axis. The carbon numbers of the molecules corresponding to these peaks were then identified and labelled.

In the second stage of the analysis, isotopic characterization of the saturate and aromatic compounds was carried out. This involved the measurement of $^{13}\text{C}/^{12}\text{C}$ ratios in individual compounds using a modified conventional isotope ratio mass spectrometer (IRMS) following initial separation by gas chromatography (GC) and carbon conversion to CO_2 in a combustion interface (hence the instrument is a GC/C/IRMS, Sano et al., 1976; Freedman et al., 1988).

Further details of the entire analytical procedure are contained in O'Malley et al. (1994).

RESULTS

Bulk geochemical analysis

Gas chromatograms were produced for both the saturate [n + iso-alkanes (paraffins) and cycloalkanes (naphthenes)] and aromatic fractions (designated PAH - polycyclic aromatic hydrocarbons - on the present chromatograms).

Saturate fraction: First of all, the analyses establish that the samples of "bitumen" are indeed the biodegraded remains of an oil phase which has reached a shallow level where it has been attacked by oxygen and bacteria. Unfortunately, gas chromatographic and isotopic analysis were made difficult because of the degraded state of the oil. The profiles of the saturate fraction of these two samples show very large background levels (often called unresolved complex mixtures or UCM) with proportionately low alkane peaks, patterns typical of degraded oils. The Bit-1 sample appears to be more highly degraded over the range C_{20} - C_{28} than the Bit-2 sample, as most of the peaks related to the individual carbon retention times are not separable from the background. In general, however, the two curves show a similar overall distribution. Because of the generally high background relative to peak levels, these molecular analyses cannot be reliably used for correlation with source rocks. The overall shape of the background curve with a maximum reached at around C_{27} - C_{28} is also characteristic of degraded oil, and attests to the preferential loss of the light ends. Minor differences are noted between the two samples: Bit-1 (test pit) appears to have preserved some of the hydrocarbons in the C_{13} - C_{14} range, with almost total loss of peaks in the C_{20} - C_{28} range, while Bit-2 (Goose Arm road) displays a more normal, albeit very subdued, distribution of original peaks.

A much more useful result was obtained for the D3-2 sample (Howley Fm.). This sample shows good preservation of peaks between C_{17} and C_{31} , with maxima in the C_{19} - C_{23} range. A very slight odd/even preference is present in the C_{25} - C_{29} range, which enables a tentative correlation with the RB-8 and RB-25 source rocks (see below). This sample, appears, however, to be depleted in components below C_{16} relative to Bit-1 and Bit-2, although this may be an artifact of the more irregular profiles of the highly degraded two latter samples.

The RB-8 and RB-25 source rock samples display slightly different saturate patterns (from each other) which suggest either a difference in their original composition or a difference in their maturation history. In particular, the abundance of the C_{17} and pristane peaks set these two samples apart, with C_{17} and pristane in RB-25 showing about twice the intensity of the surrounding peaks. Since these samples come from boreholes separated by 9 km, some compositional variation seems plausible. However, a comparison of the pristane/ C_{17} ratio with the phytane/ C_{18} ratio indicates that RB-8 is also more mature than RB-25. Furthermore, Rock-Eval data from several Rocky Brook samples in the basin by Hyde et al. (1988) show large variations in H/C along the maturation trend for Type I kerogen, thereby illustrating the range of maturation levels in the source rocks. The main similarity between the two samples is that they display a clear odd/even preference in the $\text{C}_{23}+$ range.

Aromatic Fraction: The samples Bit-1 and Bit-2 are so highly degraded that they display no usable results in the aromatic fraction.

Sample D3-2 is in a less degraded state but precision is very low with the background "hump" dominating over any of the peaks. This fraction cannot be reliably used in correlation. The general low levels of the aromatic fraction is an expected result, as the saturated fraction is generally expected to increase in proportion (relative to aromatics and asphaltenes) during migration from source rock to reservoir (Tissot, 1977).

The aromatic fraction chromatograms of the two source rocks RB-8 and RB-25 show even more pronounced differences with each other than for the saturated hydrocarbon fraction. The difference is immediately obvious in their overall profiles: RB-25 is convex upward, showing enrichment in the range C_{18} to C_{20} , while RB-8 is concave upward, showing enrichment at both ends of the C_{13} to C_{30} range.

Carbon Isotope Analysis of the Aliphatic (Saturate) Fraction

The aliphatic fraction is that fraction of hydrocarbons which form straight chains, and for the purposes of this discussion refers to the saturated hydrocarbons. The results of the $^{13}C/^{12}C$ isotopic analysis are shown in Figure 2. The purpose of such an analysis is to enable the characterization of hydrocarbons based on the origin of their carbon. These attributes are measured by the delta ^{13}C notation, which represents a convenient way to characterize carbon isotope content, and therefore can separate organic material from different environments. The heavier ^{13}C isotope is preferentially incorporated into organic material of marine origin, while the lighter ^{12}C isotope is generally partitioned into oxygenated (terrestrial) organic material. In general samples with a marine character show delta ^{13}C values in the range of -25 to -27 per mil. Hydrocarbons with a terrestrial (landplant) signature are characterized by delta ^{13}C values lighter than (i.e., less than) about -30 per mil.

In the present study, analysis of the two source rocks RB-8 and RB-25 and two bitumen samples D3-2 and Bit-2 were carried out. Only the first three of these analyses provided reliable results, however, because of the low level of confidence associated with the biodegraded Bit-2 sample. In fact, additional processing was necessary to enable this sample to be analyzed for isotopic content and although the results are included in Figure 2, this sample is assigned a low degree of reliability.

Several observations can be made from the graphed results:

- (1) the three reliable samples plot within a delta ^{13}C range of -31 to -35 per mil and suggest that these samples all came from a terrestrial environment.
- (2) not only is the bitumen sample different from the source rocks, but the two source rocks are different from each other.
- (3) the bitumen sample D3-2 and the source rock RB-8, however, display a parallel trend in their curves from C_{17} to C_{27} , despite the 2 per mil difference in the two.
- (4) all three samples show a decrease in delta ^{13}C increasing carbon number (a negative slope on the graph), which is again characteristic of terrestrially-sourced organics.

Additional laboratory processing, known as silicalite molecular sieve separation, was carried out in an attempt to render the Bit-2 sample appropriate for isotopic characterization. Two different sets of results were obtained, and this mixed result arises because of artifacts of molecular sieve fractionation.

If the normally processed Bit-2 sample is accepted and graphed we see also that between C_{15} and C_{16} (the most reliable part of the analysis, according to the precision results) the data plot in the same general area as the other samples, between -32 and -31.5 delta ^{13}C . For higher C-numbers up to C_{22} the curve moves quickly towards heavier values, but the precision level drops dramatically and the results are considered very tenuous in this range. The silicalite-processed Bit-2 sample result places the sample in the marine range in delta ^{13}C of -25 to -27 per mil. No preference can be given to either result at present.

DISCUSSION

In general, an odd number preference within n-alkanes (saturates) of high molecular weight, i.e., over the C_{27} - C_{30} range, indicates a terrestrial origin of the organic material, as, for siliciclastic sequences, odd numbers dominate in this range due to the geochemical fossils inherited from cuticular waxes of land plants and algal lipids associated with algal deposits in lacustrine environments (Tissot and Welte, 1978). However, case studies show that in ancient detrital sediment the predominance of the original odd n-alkanes of high molecular weight is preserved mainly in relatively shallow shales and silts, where degradation of kerogen has not yet started (e.g., Tissot et al., 1972; Knoche and Ourisson, 1967). With increasing maturity, an odd-even preference (also known

as CPI: carbon preference index) of about 5:1 in shallow detrital material is reduced to around unity in the zone of oil formation, as a result of thermal degradation and the introduction of new alkanes, which dilutes the original odd-even predominance (Tissot, 1977). The only slight odd/even predominance observed in the present D3-2, RB-8 and RB-25 samples is in keeping with the generally marginally mature state of many of the Rocky Brook source rocks (e.g., Kalkreuth and Macauley, 1989).

The odd carbon-numbered n-alkanes of medium molecular weight, mostly C 15 and C 17, may also represent in some cases a direct inheritance from the hydrocarbons present in algae (Tissot and Welte, 1978), considered to be the source of Type I kerogen such as is commonly associated with lacustrine deposits. For example, in upper (Mahogany) beds of the Green River shales (Robinson et al, 1965), C17 is the main n-alkane constituent in the medium molecular weight range. The Green River Formation is probably the best known oil shale deposit in the world and represents a standard to which others are compared. The comparison here serves to highlight the lacustrine/terrestrial nature of the Rocky Brook Formation, as, to the best of the authors' knowledge, most characterizations of this formation to date have been based on oil-shale stratigraphy, vitrinite reflectance, and pyrolysis, and have not used bulk geochemical analysis.

The results of the isotopic analyses suggest that no definitive correlation can be made between the one reliable bitumen sample and the source rock samples. However, the fact that they all plot with terrestrial $\delta^{13}\text{C}$ values, and that the plots display a trend towards lighter C-isotopes with increasing C-number, suggest that they are all associated with Carboniferous terrestrial depositional environments. The lacustrine origin and organic richness of the Rocky Brook shales is well known (e.g., Hyde, 1984; Kalkreuth and Macauley, 1989) and it seems likely that any oil (represented by the D3-2 bitumen) with terrestrial affinities was sourced from this potential source rock. The two RB samples also show differences in their gas chromatograph profiles, particularly in their C_{17} enrichment, which may be either related to depositional variations, or different maturation histories, or both, as noted earlier. Since source rock compositional variation is a viable option, it leaves open the possibility that the D3-2 oil was derived from an unsampled source rock within the Rocky Brook Formation, and that if a sufficiently large number of source rock samples were available, a correlation would theoretically be made. Another important point to note is that the Pr/C_{17} vs. Ph/C_{18} ratio of the D3-2 bitumen is intermediate between that of RB-8 and RB-25, which suggests strongly that the bitumen was derived from a source rock that, although not specifically represented in the two RB samples, would lay within a general population of Rocky Brook source rocks if it were available.

Although the overall geochemical results for the Bit-1 and Bit-2 samples are not definitive, the result for the D3-2 bitumen sample is encouraging. The preservation of much of the medium molecular weight saturate fraction is in strong contrast to the Goose Arm road Bit samples, and this result can be compared to that of partially degraded samples from the Seychelles as reported by Plummer (1993). This work involved the geochemical analysis and fingerprinting of tarballs which regularly wash up on beaches in the Seychelles (Indian Ocean). Plummer found that gas chromatographs for the tarballs are often depleted in alkanes in the C_{17} to C_{30} range, suggesting prolonged exposure to evaporation and/or biodegradation, thereby depleting the lighter HC fractions. However, several samples still retain a significant presence of the lighter C_{17} to C_{30} alkanes, indicative of less exposure. This result suggests that the source of this oil has been regularly replenished.

If such speculation can be applied to the Deer Lake Basin, one might say that the partially degraded D3-2 oil may represent a relatively recent phase of oil migration and emplacement at a high level in the Deer Lake Basin. Since an absolute correlation with the Rocky Brook shale source rock cannot be made, the possibility does exist that the Howley lateral basin oil was derived from a landplant source (as opposed to a lacustrine, algal source), and the present analyses provide no way to distinguish between the two terrestrial sources. Odd carbon numbered n-alkanes of high molecular weight (n-C_{25} - n-C_{33}) are found in Recent detrital sediments with an important contribution of continental runoff and comprising both clay minerals or silts and organic matter from plants. The hydrocarbons themselves are derived from cuticular waxes of the continental higher plants. Conversely, there is an absence of odd-carbon number predominance in $>\text{C}_{18}$ alkanes, even at shallow depth, in Australian Tertiary carbonate rocks with little or no contribution from continental plants (Tissot, 1978). This argues that the presence of such an odd/even predominance at all in the D3-2 sample suggests that there is a strong terrestrial signature in these rocks. A further point is that odd n-alkanes derived from higher plants occur also in oil shales like the Green River shales (Robinson et al., 1965), the Messel and Buxwiller shales in the Rhine Valley, or the Menat shales in central France with CPI ranging between 2.5 to 30 (Albrecht, 1969; Arpino, 1973). In summary, it seems likely that, based on pristane/phytane considerations, the D3-2 bitumen is derived from an oil shale source rock that has a component of terrestrial organic material in it, as evidenced by the odd/even preference of alkanes. The presence of outcropping Rocky Brook shales in southern portion of the Howley Basin and the interpretation of a depocentre from magnetic data suggest that such a source rock was available.

FUTURE STUDIES

Although this study was designed as a pilot project to test the viability of correlating these samples using basic methods, future studies of this nature could involve analysis for more specific and diagnostic compounds such as steranes, propanes and hopanes.

CONCLUSIONS

1. The bitumen samples from the Goose Arm road area at the western side of the prospect lands are the degraded remains of oils, but do not yield enough information to allow correlation with source rocks.
2. The D3-2 Howley Formation bitumen sample is less degraded than the bitumens from the western side of the basin, and likely came from a Rocky Brook source. Pristane/C₁₇ vs. phytane/C₁₈ ratios lie in an intermediate position between the two Rocky Brook source rocks, indicating that D3-2 came from a source within the general range of Rocky Brook source rocks. Isotopic characterization enables a tentative correlation with RB-8, based on a general parallelism in their plots. Finally, the general terrestrial geochemical character of D3-2, coupled with the fact that no landplant-generated Type III source rocks are known in the basin, suggests that this petroleum came from a lacustrine algal, i.e., a Rocky Brook source.
3. The two Rocky Brook samples are different from each other both in bulk composition (saturate and aromatic profiles) and in isotopic composition, but both are lacustrine in origin.
4. With regard to the prospectivity of the basin, the above results show that oil has been generated within or beneath the Carboniferous Deer Lake Basin, and has undergone some migration into fractures at the basal unconformity at the margins of the basin, and into reservoirs along the Cabot Fault system in the centre of the basin.

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Author's Note

re: Gas Chromatogram Raw Data

Raw data printouts of gas chromatographic analyses undertaken in this study have not been reproduced here but will be kept on file by the authors at the Centre for Earth Resources Research. Each data sheet includes a sample peak data table and gas chromatogram for both the saturate and aromatic fractions, as well as the specially-processed (silicalite) results.

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